PATENT ABSTRACTS OF JAPAN

(11)Publication number : 05-175030

(43)Date of publication of application : 13.07.1993

(51)Int.Cl. H01F 1/08
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(21)Application number : 03-356294

(22)Date of filing : 24.12.1991

(71)Applicant : HITACHI METALS LTD

(72)Inventor : OGAWA YOSHIKO
KOJO KATSUHIKO
EGUCHI KIYOSHI
KAWAI HIDEKI

(54) PERMANENT MAGNET

(57)Abstract:

PURPOSE: To obtain a R-T-B permanent magnet ensuring excellent corrosion resistance expanding its application field.

CONSTITUTION: A quadruple layer consisting of two double layers of Cu and Ni is provided at the surface of a R-T-B permanent magnet alloy mainly formed of a transition element T and rare earth elements R and B including yttrium.

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* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1] The permanent magnet characterized by having the 4 multistory which used as the duplex the bilayer which becomes the front face of a R-T-B system permanent magnet alloy which uses the rare earth elements R and B containing the **** element T and an yttrium as a principal component from Cu layer and nickel layer.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention is a permanent magnet which has the 4 multistory which used as the duplex the bilayer which becomes the front face of a R-T-B system permanent magnet alloy which uses the rare earth elements R and B containing the **** element T and an yttrium as a principal component from Cu layer and nickel layer, and relates to the corrosion resistance outstanding permanent magnet.
[0002]
[Description of the Prior Art] The R-T-B system permanent magnet is advantageous in respect of magnetic properties and cost, is used abundantly in the field of the electrical and electric equipment, and is going to be applied broadly increasingly. However, since it is inferior to corrosion resistance compared with a Sm-Co system magnet, it is easy to produce rust, and a R-T-B system permanent magnet may become the performance degradation of the device which incorporated the magnet by advance of rust, and the cause of contamination. Therefore, a certain surface treatment is required and surface treatment, such as bilayer plating, is carried out. For example, that to which what prepared the laminating of the base-metal layer by the noble-metals layer according [that by which what formed nickel plating with nonelectrolytic plating preferably after substrate Cu plating prepared the double layer which consists of a Cu layer and a nickel-P layer in JP,64-42805,A with nonelectrolytic plating at JP,63-318719,A] to the gaseous-phase forming-membranes method or the colloid method in JP,1-139705,A, the gaseous-phase forming-membranes method, or the nonelectrolytic-plating method has a nickel-P alloy protective layer in the 2 phase laminating condition that P contents by the nonelectrolytic-plating method differ, in JP,3-3206,A is known.
[0003]
[Problem(s) to be Solved by the Invention] The corrosion resistance of the conventional invention was inadequate. The reason is as follows. The plating film has crystalline substance structure and the growth direction is a direction perpendicular to the front face of a permanent magnet object. For this reason, it has the pinhole attained to the base of the plating film, or the substrate layer of a permanent magnet object. Therefore, seemingly, even if plating stuck, there was a problem that the moisture which dissolved the corrosion matter invaded and rust arose by the pinhole attained to a base. Furthermore, by the conventional invention, the trouble referred to as depending on the bad manufacture approach also had productivity, such as nonelectrolytic plating, the gaseous-phase forming-membranes method, and the colloid method, as above-mentioned. The permanent magnet which has a protective coat preferably producible [with electroplating] from the point of industry nature has been demanded. Then, this invention aims at offering the R-T-B system permanent magnet which solved the aforementioned technical problem and was excellent in corrosion resistance.
[0004]
[Means for Solving the Problem] In order to solve the above-mentioned trouble, this invention person found out that the permanent magnet characterized by having the 4 multistory which used as the duplex the bilayer which becomes the front face of a R-T-B system permanent magnet alloy which uses the rare earth elements R and B containing the transition metal element T and an yttrium as a principal component from Cu layer and nickel layer was excellent in corrosion resistance. That

is, this invention is a permanent magnet which has the 4 multistory which considers Cu plating as substrate plating (first pass) at the R-T-B system permanent magnet which degreased and derusted, adds Cu plating layer (the third layer) which performs nickel plating (the second layer) next and interrupts a pinhole further, and consists of nickel plating (the fourth layer) of finishing. As the first pass, in order to improve plating adhesion with a magnet object, it is desirable to perform Cu plating. The pinhole which exists in the first pass is interrupted by covering the second layer. Moreover, in order to improve the homogeneity of plating thickness, it is desirable to perform Cu plating to the third layer. The metal texture of the second layer loses a continuity by the third-layer mediation, and the third layer will be interrupted even if a pinhole grows. In addition, by as [this], since Cu which is the third layer tends to generate copper rust etc., since it is not made to goods, it finishes by the fourth layer.

[0005]

[Function] A permanent magnet like this invention intercepts the pinhole produced with Cu substrate plating with the second-layer nickel plating. Since the pinhole which links air and a material directly will be reduced if the pinhole which it cannot furthermore finish taking up with a double layer is intercepted with the third-layer Cu plating and it has nickel plating in the fourth layer, corrosion resistance becomes high.

[0006]

[Example] The ingot of a presentation of 14Nd-1Dy-7B-78Fe was obtained by the atomic ratio by casting. Coarse grinding of this ingot was carried out with the stamp mill, alloy powder with an average grain size of 3.5 micrometers was cast by the ball mill all over the magnetic field, and the molding object was acquired. This molding object was quenched after 1100 degrees C and 1-hour heating in the argon ambient atmosphere, and the sintered compact was obtained. Two steps of heat treatments, 900 degrees C and 600 degrees C, were performed for the obtained sintered compact in the argon ambient atmosphere, and the permanent magnet was obtained. The 10x10x20mm piece of a magnet was started from this permanent magnet, and it considered as the permanent magnet object. The example of a comparison when galvanizing what carried out 4 multistory plating concerning this invention to this permanent magnet object, and the double layer which is the conventional example is given.

[0007] The bath temperature at the time of plating made Cu plating 65 degrees C using electric Cu plating, using a copper sulfate bath as electric Cu plating liquid. The bath temperature at the time of plating made nickel plating 50 degrees C using electric nickel plating, using the mixed liquor of nickel-sulfate 300 g/l, nickel chloride 45 g/l, and way acid 45 g/l as an electric nickel plating liquid presentation. Plating thickness created the 4 multistory Nd-Fe-B magnet of the 20 micrometers of the total thickness of 5 micrometers of first pass electrical-and-electric-equipment Cu plating, 5 micrometers of second layer nickel plating, 5 micrometers of third layer Cu plating, and 5 micrometers of fourth layer nickel plating, and the permanent magnet of the double layer of 5 micrometers of first pass electrical-and-electric-equipment Cu plating, and 15 micrometers of the second layer of nickel plating. The metal texture of the cross section of the permanent magnet applied to this invention at drawing 1 and drawing 2 is shown. Drawing 1 is a 960 times as many optical microscope photograph as this, and drawing 2 is a 5000 times as many electron microscope photograph as this. It will be divided by the upper layer, even if it graduates with steps, and a columnar crystal organization also loses a continuity and the defect which is not desirable is made in respect of corrosion resistance, such as a pinhole, when the detailed irregularity of the sintered magnet of a substrate takes Cu-nickel-Cu-nickel and a 4 multistory configuration from drawing 2 . Thus, the PCT trial (pre shear cooker test: 120 degrees C, two atmospheric pressures) and the salt spray test (35 degrees C, 5%NaCl) estimated corrosion resistance for the obtained permanent magnet. Evaluation was performed visually. The result is shown in Table 1. The time amount indicated in Table 1 is the time amount rusting was accepted to be.

[Table 1]

---------- PCT A salt spray test ----------
---------- The 4 multistory concerning this invention > 120h > 48h ----
---------- The double layer of the example of a comparison 120h 48h ---------- It turns out that the

R-T-B system permanent magnet with which the direction which gave 4 multistory from Table 1 excelled [trial / PCT] the permanent magnet of a double layer in corrosion resistance also to any of a salt spray test is obtained.

[0008]

[Effect of the Invention] As stated above, the R-T-B system permanent magnet by this invention has the large place which contributes to expansion of an application with the outstanding corrosion resistance.

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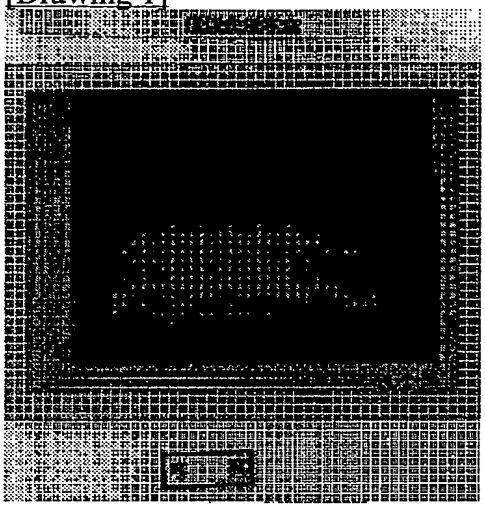
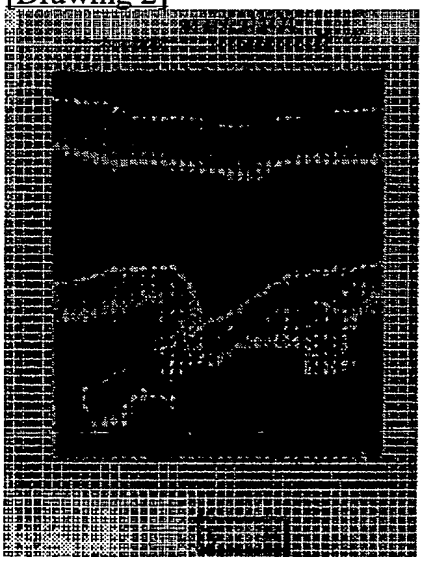
DRAWINGS

[Drawing 1]



[Drawing 2]



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	1/053					
			7371－5Ｅ	Ｈ０１Ｆ	1/ 04	Ｈ

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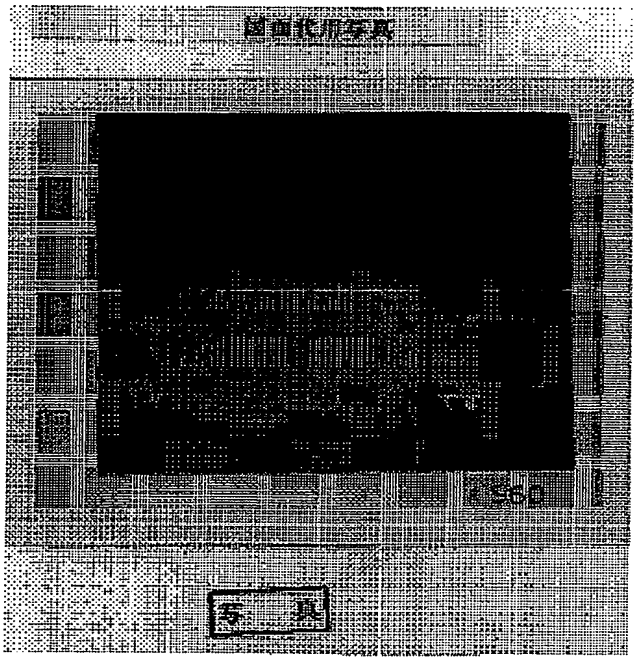
最終頁に続く

(54)【発明の名称】　永久磁石

(57)【要約】

【目的】　Ｒ－Ｔ－Ｂ系永久磁石で優れた耐食性を有するものを得て、用途の拡大に寄与すること。

【構成】　遷移元素Ｔ、イットリウムを含む希土類元素Ｒ、およびＢを主成分とするようなＲ－Ｔ－Ｂ系永久磁石合金の表面にＣｕ層およびＮｉ層からなる二層を二重にした四重層を有することを特徴とする永久磁石である。



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【特許請求の範囲】

【請求項１】　遷移元素Ｔ、イットリウムを含む希土類元素Ｒ、およびＢを主成分とするようなＲ－Ｔ－Ｂ系永久磁石合金の表面にＣｕ層およびＮｉ層からなる二層を二重にした四重層を有することを特徴とする永久磁石。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は遷移元素Ｔ、イットリウムを含む希土類元素Ｒ、およびＢを主成分とするようなＲ－Ｔ－Ｂ系永久磁石合金の表面にＣｕ層およびＮｉ層からなる二層を二重にした四重層を有する永久磁石であって耐食性の優れた永久磁石に関する。

【０００２】

【従来の技術】Ｒ－Ｔ－Ｂ系永久磁石は磁気特性、コストの点で有利であり、電気・電子機器の分野で多用されており、ますます幅広く応用されようとしている。しかし、Ｒ－Ｔ－Ｂ系永久磁石はＳｍ－Ｃｏ系磁石に比べ耐食性に劣るため錆が生じやすく、錆の進行により磁石を組み込んだ機器の性能の低下、汚染の原因となる可能性がある。そのため何らかの表面処理が必要であり、二層めっきなどの表面処理がされている。例えば、特開昭６３－３１８７１９号公報には下地Ｃｕめっきの上にＮｉめっきを好ましくは無電解めっきで設けたものが、特開昭６４－４２８０５号公報にはＣｕ層およびＮｉ－Ｐ層からなる二重層を無電解めっきで設けたものが、特開平１－１３９７０５号公報には気相成膜法あるいはコロイド法による貴金属層と気相成膜法あるいは無電解めっき法による卑金属層の積層を設けたものが、特開平３－３２０６号公報には無電解めっき法によるＰ含有量の異なる２相積層状態のＮｉ－Ｐ合金保護層を有するものが知られている。

【０００３】

【発明が解決しようとする課題】従来の発明では耐食性が不十分であった。その理由は下記の通りである。めっき膜は結晶質構造を有し、その成長方向は永久磁石体の表面と垂直な方向である。このため、めっき膜の素地または永久磁石体の下地層まで達するピンホールを有している。従って、見かけ上、めっきがついても素地まで達するピンホールによって腐食物質を溶解した水分等が侵攻し錆が生じるという問題があった。更に、上述の通り、従来の発明では無電解めっき、気相成膜法、コロイド法等の生産性が悪い製造方法に頼らざるを得ないと言う問題点もあった。工業性の点から、好ましくは電気めっき法で生産できる保護膜を有する永久磁石が要望されてきた。そこで、本発明は、前記の課題を解決し耐食性に優れたＲ－Ｔ－Ｂ系永久磁石を提供することを目的とする。

【０００４】

【課題を解決するための手段】上記問題点を解決するために、本発明者は、遷移金属元素Ｔ、イットリウムを含む希土類元素Ｒ、およびＢを主成分とするようなＲ－Ｔ－Ｂ系永久磁石合金の表面にＣｕ層およびＮｉ層からなる二層を二重にした四重層を有することを特徴とする永久磁石が耐食性に優れることを見いだした。すなわち、本発明は脱脂、除錆したＲ－Ｔ－Ｂ系永久磁石にＣｕめっきを下地めっき（第一層）とし、次にＮｉめっき（第二層）を施しさらにピンホールを中断するＣｕめっき層（第三層）を加え、仕上げのＮｉめっき（第四層）からなる四重層を有する永久磁石である。第一層として、磁石体とのめっき密着性をよくするため、Ｃｕめっきを行うことが好ましい。第一層に存在するピンホールは、第二層を被覆することにより中断される。また、めっき膜厚の均一性をよくするため、第三層にはＣｕめっきを行うことが好ましい。第三層の介在により第二層の金属組織は連続性を失い、仮にピンホールが成長したとしても第三層によって中断される。なお、第三層であるＣｕは緑青等を発生し易いため、このままでは商品にできないため、第四層で仕上げを行う。

【０００５】

【作用】本発明のような永久磁石はＣｕ下地めっきで生じるピンホールを第二層めのＮｉめっきで遮断する。さらに二重層ではふさぎきれないピンホールを第三層のＣｕめっきで遮断し、第四層めにＮｉめっきを有すると空気と素材を直結するピンホールを低減するので耐食性が高くなる。

【０００６】

【実施例】鋳造により原子比で１４Ｎｄ－１Ｄｙ－７Ｂ－７８Ｆｅの組成のインゴットを得た。このインゴットをスタンプミルで粗粉砕し，ボールミルで平均粒度３．５μｍの合金粉末を磁場中で成型して成型体を得た。この成型体をアルゴン雰囲気中で１１００℃，１時間加熱後、急冷し焼結体を得た。得られた焼結体をアルゴン雰囲気中で９００℃および６００℃の二段の熱処理を行い永久磁石を得た。この永久磁石から１０×１０×２０ｍｍの磁石片を切り出し永久磁石体とした。この永久磁石体に、本発明に係る四重層のめっきをしたものと、従来例である二重層のめっきをしたときの比較例をあげる。

【０００７】Ｃｕめっきは電気Ｃｕめっきを用い、電気Ｃｕめっき液としては硫酸銅浴を用い、めっき時の浴温は６５℃とした。Ｎｉめっきは電気Ｎｉめっきを用い、電気Ｎｉめっき液組成としては硫酸ニッケル３００ｇ／ｌ、塩化ニッケル４５ｇ／ｌ、ほう酸４５ｇ／ｌの混合液を用い、めっき時の浴温は５０℃とした。めっき膜厚は第一層電気Ｃｕめっき５μｍ、第二層Ｎｉめっき５μｍ、第三層Ｃｕめっき５μｍ、第四層Ｎｉめっき５μｍの総膜厚２０μｍの四重層のＮｄ－Ｆｅ－Ｂ磁石と、第一層電気Ｃｕめっき５μｍ、第二層のＮｉめっき１５μｍの二重層の永久磁石を作成した。図１と図２に本発明に係る永久磁石の断面の金属組織を示す。図１は９６０倍の光学顕微鏡写真、図２は５０００倍の電子顕微鏡写

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真である。図２から下地の焼結磁石の微細な凹凸がＣｕ－Ｎｉ－Ｃｕ－Ｎｉと四重層の構成をとることにより段々と平滑化され、かつ柱状晶組織も連続性を失い、仮にピンホールなどの耐食性の点で好ましくない欠陥ができても上層により分断されることになる。このようにして得た永久磁石をＰＣＴ試験（プレシャークッカーテス＊ト：１２０℃，２気圧），塩水噴霧試験（３５℃，５％ＮａＣｌ）で耐食性を評価した。評価は目視で行った。その結果を表１に示す。表１に記載された時間は発錆が認められた時間である。

【表１】

	ＰＣＴ	塩水噴霧試験
本発明に係る四重層	＞１２０ｈ	＞４８ｈ
比較例の二重層	１２０ｈ	４８ｈ

表１より四重層を施した方が二重層の永久磁石よりＰＣＴ試験も塩水噴霧試験のいずれに対しても耐食性に優れたＲ－Ｔ－Ｂ系永久磁石の得られることがわかる。

【０００８】

【発明の効果】以上述べてきたように本発明によるＲ－Ｔ－Ｂ系永久磁石は優れた耐食性を有した用途の拡大に※寄与するところが大きい。

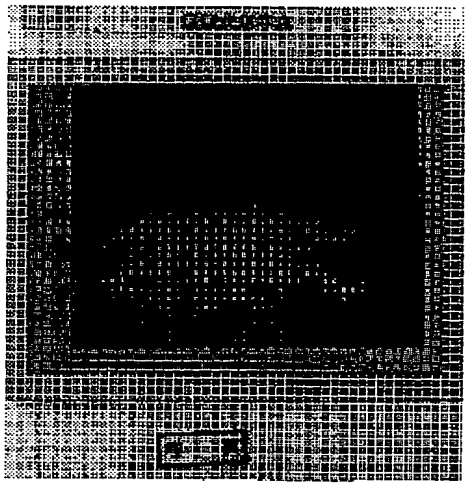
【図面の簡単な説明】

【図１】本発明に係る永久磁石の断面の金属組織を示す写真である。

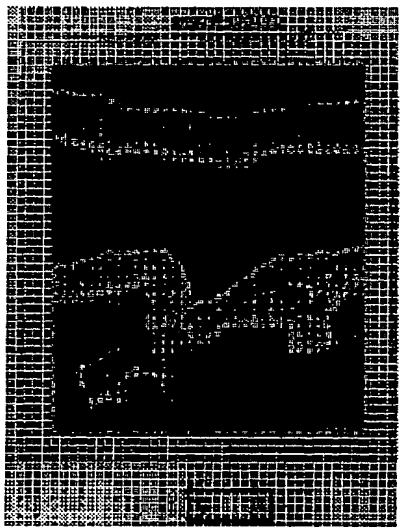
【図２】図１に示す金属組織の電子顕微鏡による部分拡大写真である。

20

【図１】



【図２】



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